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In re Application of: :

A. Nakajima et al. Art unit: 1755

Serial No. 10/647,169 :

Filed: August 21, 2003

For: INK-JET IMAGE FORMING :

METHOD

x

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and Trademarks
Washington, D.C. 20231

I, Fumio ISHII hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 252358/2002.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like

so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

A handwritten signature in cursive script, appearing to read 'Fu. Ishii', is written above a horizontal line.

Fumio ISHII

Dated: This 9th day of May, 2005.



Patent Application No. 252358/2002

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Representative: Fumio IWAI

Indication of Fee:

**Prepayment Registration
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Title of Document: Specification 1

Title of Document: Abstract 1

Necessity of Proof Required



[NAME OF DOCUMENT] SPECIFICATION

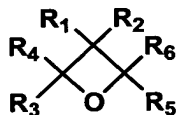
[TITLE OF THE INVENTION]

INK-JET IMAGE FORMING METHOD

[WHAT IS CLAIMED IS:]

Claim 1. An actinic radiation curable ink-jet ink comprising an oxirane group containing compound in an amount of 10 - 50 percent by weight, an oxetane ring containing compound in an amount of 50 - 90 percent by weight, and a vinyl ether compound in an amount of 0 - 40 percent by weight, an actinic radiation curable ink-jet ink wherein said oxetane ring containing compound is represented by General Formula (1) described below,

General Formula (1)



wherein $R_1 - R_6$ each represents a hydrogen atom and an organic group, and at least one of $R_3 - R_6$ is an organic group.

Claim 2. The actinic radiation curable ink-jet ink, described in claim 1, comprising further a cationic photopolymerization initiator.

Claim 3. The actinic radiation curable ink-jet ink, described in claim 1 or 2, comprising further a pigment.

Claim 4. The actinic radiation curable ink-jet ink, described in any one of claims 1 - 3, comprising further a pigment dispersing agent.

Claim 5. The actinic radiation curable ink-jet ink, described in claim 3 or 4, wherein the average particle diameter of said pigment is 10 - 150 nm.

Claim 6. The actinic radiation curable ink-jet ink, described in any one of claims 1 - 5, wherein the viscosity of said actinic radiation curable ink-jet ink is 5 - 50 mPa·s at 25 °C.

Claim 7. Printed matter which is prepared by applying onto a substrate the actinic radiation curable ink-jet ink described in any one of claims 1 - 6.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[BACKGROUND OF THE INVENTION]

The present invention relates to an actinic radiation curable ink-jet ink and printed matter using the same.

[0002]

[PRIOR ART]

Heretofore, ink-jet inks exhibiting excellent water resistance include one which is prepared by dispersing or dissolving oil-soluble dyes in high boiling point solvents,

and another which is prepared by dissolving oil-soluble dyes in volatile solvents. However, since various kinds of fastness such as lightfastness of dyes are inferior to pigments, an ink comprised of pigments, which are used as a colorant is demanded. However, it is difficult to disperse pigments into organic solvents while maintaining stability. In addition, it is difficult to realize consistent dispersibility as well as consistent ejectability. On the other hand, when an ink comprised of high boiling point solvents is applied onto a non-absorptive substrate, solvents in the aforesaid ink are not volatilized. As a result, it is difficult to dry the ink by evaporating the solvents, whereby it is impossible to result in printing on non-absorptive substrates.

[0003]

When an ink comprised of volatile organic solvents is used, it is possible to form good prints even on a non-absorptive substrate due to close adhesion property of used resins as well as volatilization of solvents. However, since volatile solvents occupy the major portion of the ink, the ink dries very rapidly on the nozzle surfaces of the head due to volatilization of the solvents. As a result, frequent maintenance is required. Further, since the ink is

substantially required for re-solubility in the solvents, sufficient durability for solvents is occasionally not achieved.

[0004]

Further, in an on-demand system printer employing a piezo element, the use of a large amount of volatile solvents increases maintenance frequency and tends to result in problems of dissolution and swelling of ink contacting materials in the printer. Further, since volatile solvents are classified as a hazardous material in the Fire Services Act, major regulations are imposed. Therefore, in the on-demand type printer employing the piezo element, it is necessary to use an ink comprised of volatile solvents in a minimal amount. However, materials which are employed to prepare the actinic radiation curable ink exhibit relatively high viscosity, whereby it has been difficult to design an ink exhibiting desired curability and stability at a viscosity capable of being ejected employing conventional printers.

[0005]

On the other hand, in order to overcome the aforesaid problems, Japanese Patent Application Open to Public Inspection No. 2002-188025 discloses an actinic radiation

curable ink-jet ink comprised of a compound having an oxirane group at the specified composition ratio, a compound having an oxetane ring, and a vinyl ether compound. The inventors of the present invention specifically studied the compounds having an oxetane ring and found the following. The aforesaid compounds and the resulting ink were relatively stable. However, the curability, the strength of the cured layer, the ejection stability at the nozzles, the close adhesion property to the substrates, the solvent resistance, and the water resistance, all resulted in problems.

[0006]

[PROBLEMS THEM PRESENT INVENTION INTENDS TO SOLVE]

An objective of the present invention is to provide an actinic radiation curable ink-jet ink which results in excellent photopolymerization, exhibits excellent curability as well as excellent stability of a compound having an oxetane ring and ink itself, results in sufficient strength of the cured layer, and exhibits ejection stability at the nozzles, excellent close adhesion property to the substrate, and excellent solvent resistance as well as water resistance, and printed matter using the same.

[0007]

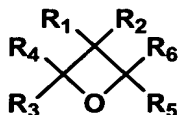
[MEANS TO SOLVE THE PROBLEMS]

An object of the present invention can be achieved by the following embodiments.

[0008]

1. An actinic radiation curable ink-jet ink comprising an oxirane group containing compound in an amount of 10 - 50 percent by weight, an oxetane ring containing compound in an amount of 50 - 90 percent by weight, and a vinyl ether compound in an amount of 0 - 40 percent by weight, an actinic radiation curable ink-jet ink wherein said oxetane ring containing compound is represented by General Formula (1) described below:

General Formula (1)



wherein $R_1 - R_6$ each represents a hydrogen atom and an organic group, and at least one of $R_3 - R_6$ is an organic group.

[0009]

2. The actinic radiation curable ink-jet ink, described in item 1, comprising further a cationic photopolymerization initiator.

[0010]

3. The actinic radiation curable ink-jet ink, described in item 1 or 2, comprising further a pigment.

[0011]

4. The actinic radiation curable ink-jet ink, described in any one of items 1 - 3, comprising further a pigment dispersing agent.

[0012]

5. The actinic radiation curable ink-jet ink, described in item 3 or 4, wherein the average particle diameter of said pigment is 10 - 150 nm.

[0013]

6. The actinic radiation curable ink-jet ink, described in any one of items 1 - 5, wherein the viscosity of said actinic radiation curable ink-jet ink is 5 - 50 mPa·s at 25 °C.

[0014]

7. Printed matter which is prepared by applying onto a substrate the actinic radiation curable ink-jet ink described in any one of items 1 - 6.

[0015]

The present invention will now be further detailed.

In the present invention, an actinic radiation curable ink-jet ink is characterized in comprising an oxirane group containing compound in an amount of 10 - 50 percent by

weight, a structure specified oxetane ring containing compound in an amount of 50 - 90 percent by weight, and a vinyl ether compound in an amount of 0 - 40 percent by weight. In the present invention, the aforesaid actinic radiation curable ink is characterized in further comprising cationic photopolymerization initiators, pigments, and pigment dispersing agents. Further, the present invention relates to the aforesaid actinic radiation curable ink characterized in that the aforesaid pigment is comprised of minute particles having an average diameter of 10 - 150 nm. Still further, the present invention relates to the aforesaid ink-jet ink characterized in that the viscosity is 5 - 50 mPa·s at 25 °C. Still further, the present invention relates to printed matter which is prepared by printing images and text onto a substrate employing the aforesaid actinic radiation curable ink-jet ink.

[0016]

Used as pigments which are incorporated into the ink-jet ink of the present invention may be achromatic inorganic pigments or chromatic organic pigments such as carbon black, titanium oxide, or calcium carbonate. Examples of organic pigments include insoluble azo pigments such as toluidine red, toluidine maroon, Hanza yellow, benzidine yellow, or

pyrazolone red; soluble azo pigments such as litol red, helio Bordeaux, pigment scarlet, or permanent red 2B; derivatives derived from vat dyes such as alizarin, indanthrone, or thioindigo maroon; phthalocyanine based organic pigments such as phthalocyanine blue or phthalocyanine green; quinacridone based organic pigments such as quinacridone red or quinacridone magenta; perylene based organic pigments such as perylene red or perylene scarlet; isoindolinone based organic pigments such as isoindolinone yellow or isoindolinone orange; pyranthrone based organic pigments such as pyranthrone red or pyranthrone orange; thioindigo based pigments; condensed azo based organic pigments; benzimidazolone based organic pigments; quinophtharone based organic pigments such as quinophtharone yellow; isoindolin based organic pigments such as isoindolin yellow; and other pigments such as flavanthrone yellow, acylamide yellow, nickel azo yellow, copper azomethine yellow, perynone orange, anthrone orange, dianthraquinonyl red, or dioxazine violet.

[0017]

Examples of organic pigments, when designated using the Color Index (C.I.) number, include C.I. Pigment Yellow 12, 13, 14, 17, 20, 24, 74, 83, 86, 93, 109, 110, 117, 125, 128, 129, 137, 138, 139, 147, 148, 150, 151, 153, 154, 155, 166,

168, 180, and 185; C.I. Pigment Orange 16, 36, 43, 51, 55, 59, and 61; C.I. Pigment Red 9, 48, 49, 52, 53, 57, 97, 122, 123, 149, 168, 177, 180, 192, 202, 206, 215, 216, 217, 220, 223, 224, 226, 227, 228, 238, and 240; C.I. Pigment Violet 19, 23, 29, 30, 37, 40, and 50; C.I. Pigment Blue 15, 15 : 1, 15 : 3, 15 : 4, 15 : 6, 22, 60, and 64; C.I. Pigment Green 7 and 36; and C.I. Pigment Brown 23, 25, and 26.

[0018]

Of the aforesaid pigments, due to excellent lightfastness, preferred are quinacridone based organic pigments, phthalocyanine based organic pigments, benzimidazolone based organic pigments, isoindolinone based organic pigments, condensed azo based organic pigments, quinophtharone based organic pigments, and isoindolin based organic pigments. The aforesaid organic pigments are preferably comprised of minute pigment particles of an average diameter of 10 - 150 nm, which is determined utilizing laser scattering. When the average particle diameter of pigments is less than 10 nm, the resulting lightfastness is degraded due to the small particle diameter. On the other hand, when it exceeds 150 nm, the stability of the resulting dispersion is lowered whereby the pigments tend to result in precipitation.

[0019]

It is possible to prepare minute-sized organic pigments, employing the method described below. Namely, a clayey mixture, consisting of at least three components of an organic pigment, a water-soluble inorganic salt in an amount of a factor of at least 3 by weight of the organic pigment, and a water-soluble solvent, is sufficiently kneaded to result in minute particles, employing a kneader and the like. Thereafter, the resulting mixture is immersed in water and stirred employing a high speed mixer to form a slurry. The resulting slurry is repeatedly filtered and washed with water, whereby water-soluble salts as well as water-soluble solvents are removed. During the minute particle production process, added may be resins as well as pigments dispersing agents. Listed as water-soluble inorganic salts are sodium chloride and potassium chloride. The weight of the employed salts is preferably in the range of 3 - 20 times the weight of the organic pigment. When the weight of the aforesaid inorganic salts is less than or equal to 3 times the organic pigment, it is impossible to prepare pigments of the desired particle size. On the other hand, when the weight is more or equal to 20 times the organic pigment, a major washing

process is required as a post-process, whereby the process amount of the organic pigments is substantially decreased.

[0020]

The aforesaid water-soluble solvents are employed so that the resulting mixture of pigments and water-soluble inorganic salts used as a crushing aid forms a suitable clayey state to result in efficient crushing. The water-soluble solvents are not particularly limited as long as they are water-soluble. However, during kneading, temperature increases, resulting in a state in which solvents tend to vaporize. As a result, from the viewpoint of safety, preferred are solvents having a boiling point of 120 -250 °C. Listed as such water-soluble solvents are 2-(methoxymethoxy)ethanol, 2-butoxyethanol, 2-(isopentyloxy)ethanol, 2-(hexyloxy)ethanol, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether, liquid polyethylene glycol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, dipropylene glycol, dipropylene glycol monomethyl ether dipropylene glycol, and low molecular weight polypropylene glycol.

[0021]

In the present invention, in order to reach sufficient concentration as well as to achieve desired lightfastness, the aforesaid pigments are incorporated in the ink-jet ink in the range of 3 - 15 percent by weight.

[0022]

Oxirane group containing compounds incorporated in the ink-jet ink of the present invention are those having, in the molecule, at least one oxirane ring represented by the formula described below.

[0023]



[0024]

It is possible to use any monomers, oligomers, or polymers which are customarily employed as an epoxy resin. Specifically listed are conventional aromatic epoxides, alicyclic epoxides, and aliphatic epoxides known in the art. Further, epoxides, as described herein, refer to monomers or oligomers. These compounds may be employed individually or if desired in combinations of at least two types.

[0025]

Preferred aromatic epoxides include di- or polyglycidyl ethers which are prepared by allowing polyhydric phenol

having at least one aromatic nucleus or alkylene oxide addition products thereof to react with epichlorohydrin. Examples include di- or polyglycidyl ethers of bisphenol A or alkylene oxide addition products thereof, di- or polyglycidyl ethers of hydrogenated bisphenol A or alkylene oxide addition products thereof, and novolak type epoxy resins. Herein, listed as alkylene oxides are ethylene oxide and propylene oxide.

[0026]

Preferred as alicyclic epoxides are compounds comprising cyclohexane oxide or cyclopentane oxide, which are prepared by epoxyfying compounds having at least one cycloalkane ring such as a cyclohexane or cyclopentane ring, employing suitable oxidizing agents such as hydrogen peroxide or peracids.

Listed as examples are;

Celoxide 2021, Celoxide 2021A, Celoxide 2021P, Celoxide 2080, Celoxide 3000, Celoxide 2000, Epolead GT 301, Epolead GT 302 Epolead GT 401, Epolead GT 403, EHPE-3150, EHPEL3150CE (Manufactured by Daicel Chemical Industries LTD.),

UVR-6105, UVR-6110, UVR-6128, UVR-6100, UVR-6216, UVR-6000 (Union Carbide Co.).

[0027]

Preferred aliphatic epoxides include di- or polyglycidyl ethers of aliphatic polyhydric alcohols or alkylene oxide addition products thereof. Representative examples include diglycidyl ethers of alkylene glycol such as diglycidyl ether of ethylene glycol, diglycidyl ether of propylene glycol, or diglycidyl ether of 6-hexanediol; polyglycidyl ethers of polyhydric alcohol such as di- or triglycidyl ethers of glycerin or alkylene oxide addition products thereof; and diglycidyl ethers of polyalkylene glycol such as diglycidyl ethers of polypropylene glycol or alkylene oxide addition products thereof. Herein, listed as alkylene oxides are ethylene oxide and propylene oxide.

[0028]

Of these epoxides, from the viewpoint of quick curability, preferred are aromatic epoxides and alicyclic epoxides and particularly preferred are alicyclic epoxides. In the present invention, the aforesaid epoxides may be employed individually or in proper combinations of at least two types.

[0029]

A compound having an oxirane group in the molecule is included in a liquid composition comprising a compound having an oxetane group (and if required admixing a vinyl ether compound) in an amount of 10 to 50 weight%, more preferably, 30 to 50 weight%.

When the amount of the oxirane compound is smaller than the above-described figure, the strength of the hardened layer becomes weak, yielding less durability of the printed materials. When the amount of the oxirane compound is larger than the above-described figure, the durability of the printed materials becomes increased, but the viscosity of the ink becomes very too high to apply to an ink-jet ink.

[0030]

Oxetane compounds of the present invention represented by aforementioned General Formula (1) incorporates one or two oxetane rings in the molecule.

[0031]

In General Formula (1), $R_1 - R_6$ each represents a hydrogen atom or a substituent, however, at least one of the groups represented by $R_3 - R_6$ is a substituent.

Examples of substituents represented by each of $R_1 - R_6$ include a fluorine atom, an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group,

or a butyl group), a fluoroalkyl group having 1 - 6 carbon atoms, an allyl group, an aryl group (e.g., a phenyl group or a naphthyl group), a furyl group, or a thienyl group. Further, these groups may have an additional substituent.

[0032]

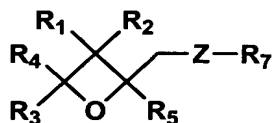
Further, of the compounds represented by aforesaid General Formula (1), preferably employed are compounds having the oxetane ring represented by General Formulas (2) - (5) described below.

[0033]

General Formula (2)



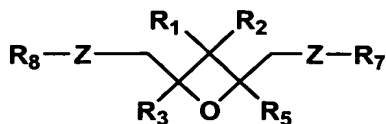
General Formula (3)



General Formula (4)



General Formula (5)



[0034]

wherein, $R_1 - R_6$ each represents a hydrogen atom or a substituent, R_7 and R_8 each represents a substituent, and Z represents an oxygen atom or a sulfur atom, or a divalent hydrocarbon group which may have an oxygen atom or a sulfur atom in the main chain.

[0035]

In General Formulas (2) - (5), $R_1 - R_6$ each represents the same substituent as that represented by each of $R_1 - R_6$ in aforesaid General Formula (1).

Examples of substituents represented by each of R_7 and R_8 include an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, or a propyl group), an alkenyl group having 1 - 6 carbon atoms (e.g., a 1-propenyl group, a 2-propenyl group, a 2-methyl-1-propenyl group, a 2-methyl-2-propenyl group, a 1-butenyl group, a 2-butenyl group, or a 3-butenyl group), an aryl group (e.g., a phenyl group or a naphthyl group), an aralkyl group (e.g., a benzyl group, a fluorobenzyl group, or a methoxybenzyl group), an acyl group having 1 - 6 carbon atoms (e.g., a propylcarbonyl group, a butylcarbonyl group, or a pentylcarbonyl group), an alkoxy carbonyl group having 1 - 6 carbon atoms (e.g., an ethoxycarbonyl group, a propoxycarbonyl group, or a

butoxycarbonyl group), an alkylcarbamoyl group having 1 - 6 carbon atoms (e.g., a propylcarbamoyl group or a butylpentylcarbamoyl group), and an alkoxycarbamoyl group (e.g., an ethoxycarbamoyl group).

In General Formulas (2) and (4), at least one of R_3 to R_6 is an organic group described above.

[0036]

Examples of a divalent hydrocarbon group represented by Z, which may contain an oxygen atom or a sulfur atom in the main chain, are: an alkylene group (e.g., an ethylene group, a trimethylene group, a tetramethylene group, a propylene group, an ethylethylene group, a pentamethylene group, a hexamethylene group, a heptamethylene group, an octamethylene group, nonamethylene group, or a decamethylene group); an alkenylene group (e.g., a vinylene group or a propenylene group); and an alkynylene group (e.g., an ethynylene group or a 3-pentynylene group).

[0037]

Regarding oxetane compounds used in the present invention, R_1 is preferably a lower alkyl group. Specifically, the ethyl group of these is preferably employed. Further, either R_7 or R_8 is preferably a propyl group, a butyl group, a phenyl group, or a benzyl group,

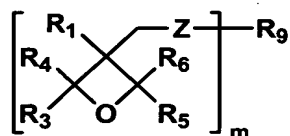
while Z is preferably a hydrocarbon group having neither an oxygen atom nor a sulfur atom.

[0038]

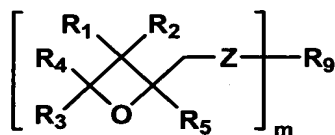
Compounds having at least two oxetane rings in the molecule are represented by General Formulas (6) and (7) described below.

[0039]

General Formula (6)



General Formula (7)



[0040]

wherein m represents 2, 3, or 4; Z is the same as the groups used in aforesaid General Formulas (2) - (5); $R_1 - R_6$ each represents a hydrogen atom or an organic group, the organic group being the same as $R_1 - R_6$ in General Formula (1). In General Formula (6), at least one of $R_3 - R_6$ is the aforementioned organic group

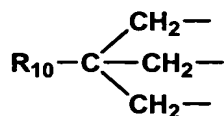
[0041]

R₉ represents a straight or branched alkylene group having 1 - 12 carbon atoms, a straight or branched poly(alkyleneoxy) group or a divalent group selected from the group consisting of General Formulas (9), (10), and (11) described below.

Preferably employed as the aforesaid branched alkylene group having 1 - 12 carbon atoms are alkylene groups represented by General Formula (8) described below.

[0042]

General Formula (8)

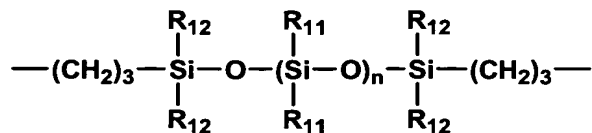


[0043]

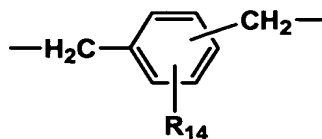
In General Formula (8), R₁₀ represents a lower alkyl group (e.g., a methyl group, an ethyl group, or a propyl group).

[0044]

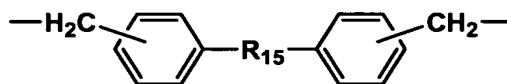
General Formula (9)



General Formula (10)



General Formula (11)

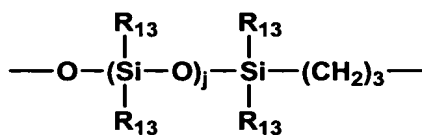


[0045]

In General Formula (9), n represents 0 or an integer of 1 - 2,000, R_{12} represents an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group), and or the group represented by General Formula (12) described below.

[0046]

General Formula (12)



[0047]

In General Formula (12), j represents 0 or an integer of 1 - 100, and R_{13} represents an alkyl group having 1 - 10 carbon atoms.

[0048]

R_{12} represents an alkyl group having 1 - 10 carbon atoms such as a methyl group, an ethyl group, a propyl group, or a butyl group.

[0049]

In General Formula (10), R_{14} represents a hydrogen atom or an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group), an alkoxy group having 1 - 10 carbon atoms, a halogen atom, a nitro group, a cyano group, a mercapto group, an alkoxy carbonyl group having lower alkyl group, or a carboxyl group.

[0050]

In General Formula (11), R_{15} represents an oxygen atom, a sulfur atom, $-NH-$, $-SO-$, $-SO_2-$, $-CH_2-$, $-C(CH_3)_2-$, or $-C(CF_3)_2-$.

[0051]

Preferred oxetane compounds used in the present invention are as follows. For example, in aforesaid General Formulas (6) and (7), R_1 is preferably a lower alkyl group, more preferably an ethyl group, and R_9 is a hexamethyl group. In aforesaid General Formula (10), preferably employed is a compound in which R_{14} is a hydrogen atom.

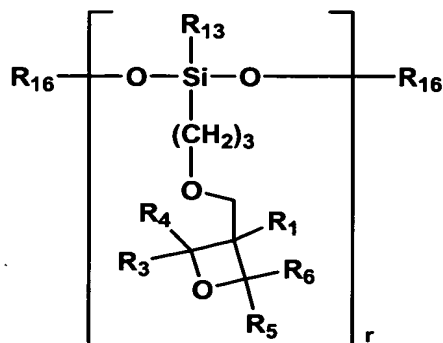
In aforesaid General Formula (8), it is preferable that R_{10} is an ethyl group. In aforesaid General Formulas (9) and (12), R_{12} and R_{13} each is a methyl group, and Z is a hydrocarbon group which contains neither an oxygen atom nor a sulfur atom.

[0052]

Further, listed as one example of preferred embodiments of compounds having an oxetane ring according to the present invention is the compound represented by General Formula (13) described below.

[0053]

General Formula (13)



[0054]

In General Formula (13), r represents an integer of 25 - 200; R_1 , $R_3 - R_6$, and R_{13} each is the same as a substituent described in aforesaid General Formula. R_{16} represents an alkyl group having 1 - 4 carbon atoms or a trialkylsilyl

group; however, at least one of $R_3 - R_6$ is an organic group described above.

[0055]

Specific examples of oxetane compounds used in the present invention can be prepared by considering the following references.

[0056]

- (1) Hu Xianming, Richard M. Kellogg, *Synthesis*, 533 - 538, May (1995)
- (2) A. O. Fitton, J. Hill, D. Ejane, R. Miller, *Synth.*, 12, 1140 (1987)
- (3) Toshiro Imai and Shinya Nishida, *Can. J. Chem.* Vol. 59, 2503 - 2509 (1981)
- (4) Nobujiro Shimizu, Shintaro Yamaoka, and Yuho Tsuno, *Bull. Chem. Soc. Jpn.*, 56, 3853 - 3854 (1983)
- (5) Walter Fisher and Cyril A. Grob, *Helv. Chim. Acta.*, 61, 2336 (1987)
- (6) *Chem. Ber.* 101, 1850 (1968)
- (7) "Heterocyclic Compounds with Three- and Four-membered Rings", Part Two, Chapter IX, Interscience Publishers, John Wiley & Sons, New York (1964)
- (8) *Bull. Chem. Soc. Jpn.*, 61, 1653 (1988)
- (9) *Pure Appl. Chem.*, A29 (10), 915 (1992)

(10) Pure Appl. Chem., A30 (2 & amp;3), 189 (1993)

(11) Japanese Patent Application Open to Public Inspection
No. 6-16804

(12) DE 10221858

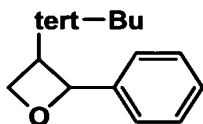
[0057]

Exemplified compounds were synthesized as shown in examples, based on the aforesaid publications.

Exemplified Compound 1: trans-3-butyl-2-phenoloxetane

[0058]

Exemplified Compound 1



[0059]

Potassium hydroxide was added to a methanol solution of benzaldehyde, and 3-dimethyl-butyraldehyde, and diol was prepared utilizing the Cross Cannizzaro reaction. Subsequently, a dichloromethane solution of methanesulfonyl chloride was dripped into a dichloromethane, diol and dried triethylamine solution at 0 °C. Stirring was continued at 40 °C for 30 minutes, and for an additional one hour at room temperature. The resulting mixture was washed with water, and a citrate compound was recrystallized employing

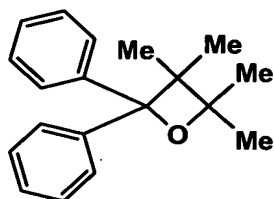
dichloromethane. Subsequently, tetrabutylammonium hydrogen sulfate was added and sodium hydroxide was dripped at room temperature. The resulting mixture underwent reaction for 24 hours. The reaction product was washed with water, dehydrated by anhydrous sodium sulfate and then subjected to vacuum distillation, whereby a targeted compound was prepared.

[0060]

Exemplified Compound 2: 3,3,4,4-tetramethyl-2,2-diphenyloxetane

[0061]

Exemplified Compound 2



[0062]

A benzene solution of benzophenone and 2,3-dimethyl-2-butene was placed in a photochemical reaction apparatus made of Pyrex (registered trade mark) into which argon was sealed, and while stirring, was exposed to ultraviolet radiation for 12 hours, employing a high pressure mercury lamp. After

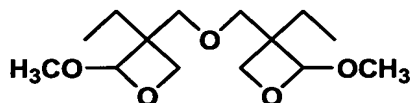
removing solvents, vacuum distillation was carried out, whereby a targeted compound was prepared.

[0063]

Exemplified Compound 3: di[3-ethyl(2-methoxy-3-oxetanyl)]methyl ether

[0064]

Exemplified Compound 3



[0065]

A mixture consisting of 2-ethyl-2-[2-(hydroxy-methoxy-methyl)-2-hydroxymethyl-butoxymethyl]-1-methoxy-propane-1,3-diol, diethyl carbonate, and potassium carbonate was refluxed until the temperature decreased to a maximum of 120 °C. The resulting mixture was subjected to vacuum distillation while maintaining the temperature at 76 - 78 °C, whereby a targeted compound was prepared.

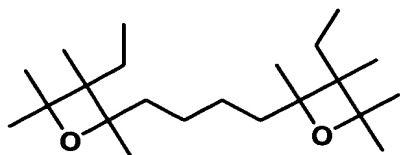
Exemplified Compound 3: di[3-ethyl(2-methoxy-3-oxetanyl)]methyl ether

[0066]

Exemplified Compound 4: 1,4-bis(2,3,4,4-tetramethyl-3-ethyl-oxetanyl)butene

[0067]

Exemplified Compound 4



[0068]

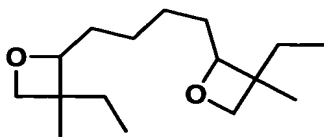
A mixture consisting of 3,10-diethyl-2,3,4,9,11-hexamethyl-dodecane-2,3,4,9,11-tetraol, diethyl carbonate, and potassium carbonate was refluxed until the temperature decreased to a maximum of 120 °C. The resulting mixture was subjected to vacuum distillation while maintaining the temperature at 74 - 76 °C, whereby a targeted compound was prepared.

[0069]

Exemplified Compound 5: 1,4-bis(3-methyl-3-ethyl-oxetanyl)butene

[0070]

Exemplified Compound 5



[0071]

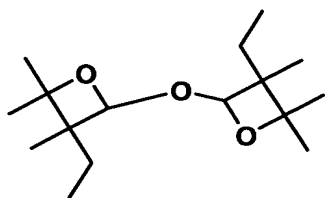
A mixture consisting of 2,9-diethyl-2,9-dimethyl-decane-1,3,8,10-tetraol, diethyl carbonate, and potassium carbonate was refluxed until the temperature decreased to a maximum of 120 °C. The resulting mixture was subjected to vacuum distillation while maintaining the temperature at 70 - 72 °C, whereby a targeted compound was prepared.

[0072]

Exemplified Compound 6: di(3,4,4-trimethyl-3-ethyl-oxetanyl)methyl ether

[0073]

Exemplified Compound 6



[0074]

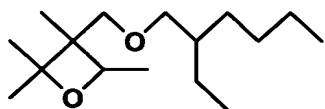
A mixture consisting of 3-ethyl-1-(2-ethyl-1,3-dihydroxy-2,3-dimethyl-butoxy)-3,4-dimethyl-pentene-2,4,-diol, diethyl carbonate, and potassium carbonate was refluxed until the temperature decreased to a maximum of 120 °C. The resulting mixture was subjected to vacuum distillation while maintaining the temperature at 80 - 82 °C, whereby a targeted compound was prepared.

[0075]

Exemplified Compound 7: 3-(2-ethyl-hexyloxymethyl)-2,2,3,4-tetramethyl-oxetane

[0076]

Exemplified Compound 7



[0077]

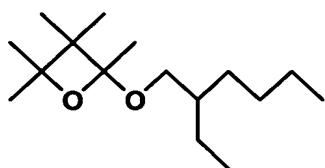
While stirring, tetra-n-butylammonium bromide was dripped in an aqueous (2,2,3,4)-tetramethyl-oxetan-3-yl)-methanol 1-bromo-2-ethylhexyl solution and an aqueous potassium hydroxide solution. After 24 hours, methylene chloride and water were added. The resulting organic phase was washed with water, then washed with magnesium sulfate, and finally filtered. Subsequently, solvents were removed and vacuum distillation was carried out, whereby a targeted compound was prepared.

[0078]

Exemplified Compound 8: 2-(2-ethyl-hexyloxy)-2,3,3,4,4-pentamethyl-oxetane

[0079]

Exemplified Compound 8



[0080]

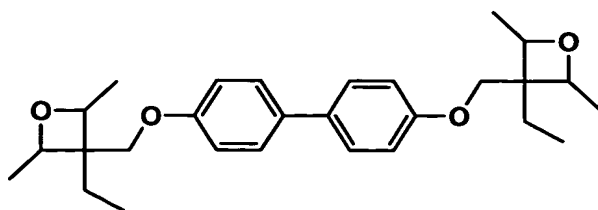
While stirring, tetra-n-butylammonium bromide was added to a 2,3,3,4,4-pentamethyl-oxetane-2-ol 1-bromo-2-ethylhexyl solution and an aqueous potassium hydroxide solution. After 24 hours, methylene chloride and water were added. The resulting organic phase was washed with water, then dehydrated employing magnesium sulfate, and finally filtered. Subsequently, solvents were removed and vacuum distillation was carried out, whereby a targeted compound was prepared.

[0081]

Exemplified Compound 9: 4,4'-bis[(2,4-dimethyl-3-ethyl-3-oxetanyl)methoxy]biphenyl

[0082]

Exemplified Compound 9



[0083]

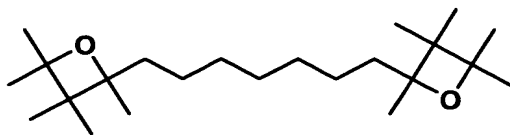
While heated at 80 °C, 3-chloromethyl-3-ethyl-2,4-dimethyl-oxetne, 4,4'-biphenol, and tetra-butylphosphonium bromide were stirred. Subsequently, an aqueous potassium hydroxide solution was dripped into it. The resulting mixture was heated (to approximately 110 °C) to initiate refluxing and underwent reaction for 8 hours while refluxed. After the reaction, the reacted mixture was cooled to room temperature. Subsequently pure water was added. After stirring well, deposits were collected by filtration. The resulting deposits were washed with water and then washed with methanol. Subsequently, drying was carried out employing a vacuum dryer, whereby a targeted compound was prepared.

[0084]

Exemplified Compound 10: 7-bis(2,3,3,4,4-pentamethyl-oxetanyl;)heptane

[0085]

Exemplified Compound 10



[0086]

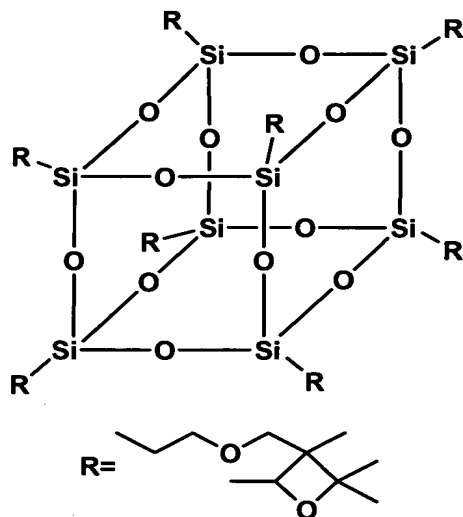
A mixture consisting of 2,12-diethyl-2,12-dimethyl-tridecane-1,3,11,13-tetraol, diethyl carbonate, and potassium carbonate was refluxed until the temperature decreased to a maximum of 120 °C. The resulting mixture was subjected to vacuum distillation while maintaining the temperature at 80 - 82 °C, whereby a targeted compound was prepared.

[0087]

Exemplified Compound 11: oxetanyl silsesquioxanes

[0088]

Exemplified Compound 11

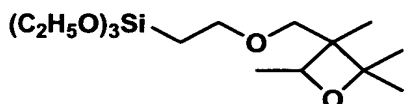


[0089]

Isopropyl alcohol, an aqueous tetramethylammonium hydride solution and water were charged, and the oxetane compound described below was gradually added. The resulting

mixture was stirred at room temperature for 24 hours and subsequently was allowed to stand. After the reaction, toluene was added to the system and the reaction solution was washed with an aqueous sodium chloride saturated solution, employing a separating funnel. Water washing was repeated until the water layer in the separating funnel became neutral. Thereafter, the organic layer was collected and dehydrated employing anhydrous sodium sulfate. Thereafter, toluene was distilled out under vacuum, whereby a targeted compound was prepared.

[0090]



[0091]

In the present invention, the composition may be comprised of at least two oxetane compounds having at least one oxetane ring in the molecule. Further, at the same time, it is possible to use prior art compounds having oxetane ring(s), described in Japanese Patent Application Open to Public Inspection Nos. 2001-181386, 2000-256571, 10-204072, 11-24654, 2000-86646, 2000-302774, 2002-20376, 8-143806, 11-322735, 2000-1482, 2001-220526, and 2002-188025.

[0092]

The aforesaid oxetane ring containing compounds are incorporated in the liquid component comprised of vinyl ether compounds in an amount of 50 - 90 percent by weight and preferably 50 - 70 percent by weight. When the amount of the oxetane ring containing compounds is less than the lower limit, the resulting curability is degraded, while when it exceeds the upper limit, the resulting curability is improved but durability of printed matter is not achieved due to the insufficient strength of the cured layer.

[0093]

Examples of vinyl ether compounds include di- or trivinyl ether compounds such as ethylene glycol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, propylene glycol divinyl ether, dipropylene glycol divinyl ether, butanediol divinyl ether, hexanediol divinyl ether, cyclohexanedimethanol divinyl ether, and trimethylolpropane trivinyl ether, and monovinyl ether compounds such as ethyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, octadecyl vinyl ether, cyclohexyl vinyl ether, hydroxybutyl vinyl ether, 2-ethylhexyl vinyl ether, cyclohexanedimethanol monovinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, isopropenyl ether-O-propylene

carbonate, dodecyl vinyl ether, diethylene glycol monovinyl ether, and octadecyl vinyl ether.

[0094]

Of these vinyl ether compounds, when taking into account curability, adhesion properties, and surface hardness, di- or trivinyl ether compounds are preferred, and divinyl ether compounds are particularly preferred. In the present invention, the aforesaid vinyl ether compounds may be employed individually or in combinations of at least two types.

[0095]

The aforesaid vinyl ether compounds are employed as an optional blending component. However, through their incorporation, it is possible to decrease the viscosity of the ink-jet ink to the desired level. Further, it is possible to enhance the curing rate. The vinyl ether compounds are incorporated into the liquid component comprised of oxirane group containing compounds and oxetane ring containing compounds in an amount of 0 - 40 percent by weight or preferably 0 - 20 percent by weight.

[0096]

Listed as cationic photopolymerization initiators are arylsulfonium salt derivatives (e.g., Cyracure UVI-6990 and

Cyracure UVI-6974, manufactured by Union Carbide Co., and Adeka Optomer SP-150, Adeka Optomer SP-152, Adeka Optomer SP-170, and Adeka Optomer SP-172, manufactured by Asahi Denka Kogyo Co.), allyliodonium salt derivatives (e.g., RP-2074, manufactured by Rohdia Co.), allene-ion complex derivatives (e.g., Irugacure 261, manufacture by Ciba-Geigy Limited), diazonium salt derivatives, triazine based initiators, and others such as acid generating agents such as halides. The aforesaid cationic photopolymerization initiators are preferably incorporated in an amount of 0.2 - 20 parts by weight with respect to 100 parts by weight of the compound having an alicyclic epoxy group. When the amount of the cationic photopolymerization initiators is less than 0.2 part by weight, it is difficult to prepare cured materials. On the other hand, the incorporation in an amount exceeding 20 parts by weight results in no curability enhancing effects. These cationic photopolymerization initiators may be employed individually or in combinations of at least two selected types.

[0097]

Listed as photopolymerization promoters are anthracene and anthracene derivatives (e.g., Adeka Optomer SP-100, manufactured by Asahi Denka Kogyo Co.). These

photopolymerization promoters may be employed individually or in combinations of a plurality of types.

[0098]

Listed as pigment dispersing agents may be carboxylic acid esters containing a hydroxyl group, salts of long chain polyamides with high molecular weight acid esters, high molecular weight polycarboxylic acid salts, salts of long chain polyaminoamides with polar acid esters, high molecular weight unsaturated acid esters, high molecular copolymers, modified polyurethanes, modified polyacrylates, polyether ester type anion based surfactants, naphthalenesulfonic acid formalin condensation product salts, aromatic sulfonic acid formalin condensation product salts, polyoxyethylene alkylphosphoric acid esters, polyoxyethylene nonyl phenyl ether, stearylamine acetate, and pigment derivatives.

[0099]

Specific examples of pigment dispersing agents include "Anti-Terra-U (a polyaminoamide phosphoric acid salt)", "Anti-Terra-203/204 (a high molecular weight epoxycarboxylic acid salt)", "Disperbyk-101 (polyaminoamide phosphoric acid salt and acid ester), 107 (a hydroxyl group containing carboxylic acid ester), 110 (an acid group containing copolymer), 130 (polyamide), 161, 162, 163, 164, 165, 166,

and 170 (high molecular copolymer)", "400", "Bykumen" (a high molecular weight unsaturated acid ester), "BYK-P104, P105 (high molecular weight unsaturated polycarboxylic acid)" "P104S, 240S (high molecular weight unsaturated acid polycarboxylic acid and silicon based), and "Lactimon (long chain amine, unsaturated acid polycarboxylic acid, and silicon)", manufactured by BYK Chemie Co.

[0100]

Further, listed are "Efka 44, 46, 47, 48, 49, 54, 63, 64, 65, 66, 71, 701, 764, and 766", "Efka Polymer 100 (modified polyacrylate), 150 (an aliphatic modified polymer), 400, 401, 402, 403, 450, 451, 452, and 453 (modified polyacrylates), 745 (being copper phthalocyanine based)", manufactured by Efka Chemicals Co., and "Flowlen TG-710 (urethane oligomer)", "Flownon SH-290, SP-1000", "Polyflow No. 50E, and No. 300 (an acryl based copolymer)", manufactured by Kyoei Kagaku Co., "Disparlon KS-860, 873SN, and 874 (a polymer dispersing agent), #2150 (aliphatic multivalent carboxylic acid), and #7004 (polyether ester type)", manufactured by Kusumoto Kasei Co.

[0101]

Further, listed are "Demol RN and N (both are naphthelenesulfonic acid formalin condensation product sodium

salts), MS, C, and SN-B (all are aromatic sulfonic acid formalin condensation product sodium salts), and EP", "Homogenol L-18 (a polycarboxylic acid type polymer)", "Emulgen 920, 930, 931, 935, 950, and 985 (all are polyoxyethylene nonyl phenyl ethers)", and "Acetamin 24 (coconut amine acetate) and 86 (stearylamine acetate)", manufactured by Kao Corp., "Solsperse 5000 (phthalocyanine ammonium salt based), 13240 and 13940 (both are polyesteramine based), 17000 (being fatty acid amine based), 24000, and 2000", manufactured by Zeneca Corp., and "Nikkol T106 (polyoxyethylene sorbitan monooleate), MYS-IEX (polyoxyethylene monostearate), and Hexagline 4-O (hexaglyceryl tetraoleate)", manufactured by Nikko Chemical Co.

[0102]

The aforesaid pigment dispersing agents are preferably incorporated in an amount ranging from 0.1 to 10 percent by weight in the ink.

[0103]

The ink-jet ink of the present invention is produced by dispersing pigments together with actinic radiation curable compounds and pigment dispersing agents, employing a common homogenizer such as a sand mill. It is preferable that a

concentrated liquid pigment composition at a high concentration, which has previously been prepared, is diluted by actinic radiation curable compounds. It is possible to achieve sufficient dispersion even though dispersion is carried out employing a common homogenizer. Due to that, excessive dispersion energy as well as excessive dispersion time is not needed. As a result, ink components are not easily modified during dispersion, whereby it is possible to prepare an ink which exhibits excellent stability. The ink is preferably filtered employing a filter having a pore size of at most 3 μm and further at most 1 μm .

[0104]

The viscosity of the ink-jet ink of the present invention is preferably adjusted to 5 - 50 $\text{mPa}\cdot\text{s}$ at 25 °C, which is relatively high. The ink at a viscosity of 5 - 50 $\text{mPa}\cdot\text{s}$ at 25 °C exhibits consistent ejection characteristics when ejected from a head having a common frequency of 4 - 10 KHz as well as from a head having a high frequency of 10 - 50 KHz. When the aforesaid viscosity is less than 5 $\text{mPa}\cdot\text{s}$, in the high frequency head, ejection responding properties are noticeably degraded. On the other hand, when it exceeds 50 $\text{mPa}\cdot\text{s}$, even though a viscosity decreasing mechanism employing heating is installed in the head, ejection itself is lowered,

and ejection stability is lost, whereby it becomes impossible to achieve stable ejection.

[0105]

Further, when a piezo head is used, the conductivity of the ink-jet ink of the present invention is preferably adjusted to at most 10 $\mu\text{S}/\text{cm}$ to minimize electrolytic corrosion of the interior of the head. Further, in a continuous type, it is necessary to adjust the conductivity by the use of electrolytes. In such a case, it is necessary to adjust the conductivity to at least 0.5 mS/cm .

[0106]

Substrates employed in the present invention include all the conventional synthetic resins which are widely employed for various uses. Specific examples include polyester, polyvinyl chloride, polyethylene, polyurethane, polypropylene, acrylic resins, polycarbonate, polystyrene, acrylonitrile-butadiene-styrene copolymers, polyethylene terephthalate, and polybutadiene terephthalate. The thickness and shape of these synthetic resinous substrates are not particularly limited.

[0107]

The ink-jet ink of the present invention is used as follows. Initially, the aforesaid ink-jet ink is supplied to

the printer head of a printer for the ink-jet recording system and is ejected onto a substrate from the aforesaid printer head. Thereafter, it is exposed to actinic radiation such as ultraviolet radiation or electron beams. By such radiation, the ink composition on a printing medium undergoes rapid curing.

[0108]

Incidentally, when ultraviolet radiation is used as exposure radiation, employed as actinic radiation sources may be, for example, mercury arc lamps, xenon arc lamps, fluorescent lamps, carbon arc lamps, tungsten-halogen copying lamps, and sun light. When curing is carried out employing electron beams, commonly used as beams are those with an energy of at most 300 eV. However, it is possible to carry out instantaneous curing at an exposure amount of 1 - 5 Mrad.

[0109]

[EXAMPLES]

The present invention will now be described based on examples. However, the present invention is not limited thereto.

[0110]

(Preparation Of Present Invention Inks 1 - 8)

The pigment, dispersing agent, oxirane group containing compound, oxetane ring containing compound, and vinyl ether compound, shown in Table 1, were all charged into a sand mill and dispersed for 4 hours, whereby an actinic radiation curable ink composition was prepared. Subsequently, a photoinitiator was added to the aforesaid composition, and slowly mixed until the aforesaid photoinitiator was dissolved. Thereafter, the resulting mixture was filtered under pressure employing a membrane filter, whereby an actinic radiation curable ink-jet ink was prepared. The resulting ink was loaded into an ink-jet printer, having a piezo head, and printing was performed on polyethylene terephthalate film. Subsequently, curing was carried out at a substrate conveyance rate of 500 mm/second, employing a UV exposure apparatus (8 cold cathode tubes: 20 W output).

Table 1

Present Invention Ink		1	2	3	4	5	6	7	8
Pigment	P1	5	5						
	P2			5	5				
	P3					5	5		
	P4							5	5
Oxirane Containing Compound	Celoxide 3000	50	20	5	10	20	10	40	40
	Celoxide 2021 P		10	10		10	20		5
	Exemplified Compound 1			50					80
Oxetane Ring Containing Compound	Exemplified Compound 2	90	70				90		
	Exemplified Compound 3				50	60		70	
	DVE-3	10	40	40	10		40	10	20
Initiator	Pigment Dispersing Agent	3	3	3	3	3	3	3	3
	SP-152	10					10		
	SP-172				10	10			10
	UVI6990		10	10				10	

[0112]

Compounds in Table 1 are described below. The numerical figure represents the number of parts.

Pigment

P1: 250 parts of crude copper phthalocyanine ("Copper Phthalocyanine", manufactured by Toyo Ink Co.), 2,500 parts of sodium chloride, and 160 parts of polyethylene glycol ("Polyethylene Glycol 300", manufactured by Tokyo Kasei Co.), were charged in a 1-gallon styrene kneader (manufactured by Inoue Seisakusho Co.) and kneaded for 3 hours. Subsequently, the resulting mixture was charged into 2.5 L of heated water, and the resulting mixture was stirred for approximately one hour while heated to approximately 80 °C to form a slurry. Thereafter, the resulting slurry was filtered, washed with water 5 times to remove sodium chloride and solvents, and spray-dried, whereby a dried processing pigment was prepared. Subsequently, a processing pigment was prepared in the same manner as P1.

[0113]

P2: 250 parts of quinacridone based red pigment ("Sincasia Magenta RT-355-D), manufactured by Ciba-Geigy Ltd.), 2,500 parts of sodium chloride, and 160 parts of polyethylene glycol ("Polyethylene Glycol 300", manufactured by Tokyo

Kasei Co.) were charged into a 1-gallon styrene kneader. A processing pigment was then prepared in the same manner as P1.

[0114]

P3: 250 parts of benzimidazolone based pigment ("Fosterperm Yellow H3G", manufactured by Hoechst Co.), 2,500 parts of sodium chloride, and 160 parts of polyethylene glycol ("Polyerthylene Glycol 300", manufactured by Tokyo Kasei Co.) were charged into a 1-gallon styrene kneader. A processing pigment was then prepared in the same manner as P1.

[0115]

P4: carbon black pigment "Printex 150T" (manufactured by Degusa Corp.)

Oxirane group containing compound

Celoxide 3000: alicyclic epoxy (manufactured by Daiseru Co.)

Celoxide 2021P: alicyclic epoxy (manufactured by Daiseru Co.)

Vinyl ether compound

DVE-3: triethyleneglycol divinyl ether (manufactured by ISP Co.)

Pigment dispersing agent

32000: modified aliphatic dispersing agent ("Solsperse 32000, manufactured by Zeneca Co.)

Initiator

SP-152: triphenylsulfonium salt (Adeka Optomer SP-152, manufactured by Asahi Denka Co.)

Sp-172: triphenylsulfonium salt (Adeka Optomer SP-170, manufactured by Asahi Denka Co.)

UV16990: triphenylsulfonium salt ("Cylacure UVI-6990", manufactured by Union Carbide Co.)

(Preparation of Comparative Inks 1 - 8)

A pigment, dispersing agent, and monomer were charged into a sand mill and dispersed for 4 hours, whereby a liquid actinic radiation curable ink-jet ink composition was prepared. Subsequently, a photoinitiator was added to the aforesaid liquid ink composition and mixed slowly until the aforesaid photoinitiator was dissolved. Thereafter, the resulting mixture was filtered under pressure employing a membrane filter, whereby an actinic radiation curable ink-jet ink was prepared. The resulting ink was loaded into an ink-jet printer, having a piezo head, and printing was performed onto the aforesaid substrate. Subsequently, curing was carried out at a substrate conveyance rate of 500 mm/second, employing a UV exposure apparatus (8 cold cathode tubes: 20 W output).

[0116]

Table 2

Comparative Ink		1	2	3	4	5	6	7	8
Pigment	P1	5	5						
	P2			5	5				
	P3					5	5		
	P4							5	5
Oxirane Containing Compound	Celoxide 3000	50	20	5	10	20	10	40	40
	Celoxide 2021 P		10	10		10	20		5
Oxetane Ring Containing Compound	OXT-121			50					80
	OXT-211	90	70				90		
	OXT-101				50	60		70	
Vinyl Ether Compound	DVE-3	10	40	40	10		40	10	20
Pigment Dispersing Agent	32000	3	3	3	3	3	3	3	3
Initiator	SP-152	10					10		
	SP-172				10	10			10
	UVI6990		10	10				10	

[0117]

Employed as compounds in Table 2, except for oxetane ring containing compounds described below, were the same compounds used in Present Invention Inks 1 - 8.

[0118]

Oxetane Ring Containing Compounds

OXT-121: 1,4-bis{[(3-ethyl-3-oxetanyl)methoxy]methyl}benzene
(manufactured by Toa Gosei Co.)

OXT-211: 3-ethyl-3-(phenoxymethyl)oxetane (manufactured by
Toa Gosei Co.)

OXT-101: 3-ethyl-3-hydroxymethyloxetane (manufactured by Toa
Gosei Co.)

Present Invention Inks 1 - 8 and Comparative Inks 1 - 8, as well as printed matter prepared by those inks were evaluated as described below. Table 3 shows the results.

[0119]

Evaluation methods for items described in Table 3 are as follows.

Curability: the number of passes of the conveyor UV lamp until no tackiness was felt manually

Stability (oxetane ring containing compounds): after the oxetane ring containing compound was stored at 100 °C for one

month, the resulting dispersion state was visually evaluated and any viscosity change was also noted for evaluation.

[0120]

A: No viscosity change was noticed

B: Increase in viscosity was noticed

C: Generation of gelled materials was noticed

[0121]

Stability (ink): After storing the ink at 25 °C for one month, its dispersion state was visually evaluated, and any viscosity change was also noted for evaluation.

[0122]

A: No formation of precipitates was noticed, resulting in no viscosity change

B: No formation of precipitates was noticed, resulting in a slight decrease in the viscosity

C: Formation of precipitates was noticed

[0123]

Stability (ejection): After continuous ink ejection for 30 minutes, the presence and absence of no ejection nozzles was observed and continuous ejectability was evaluated based on the criteria below.

[0124]

A: During 30-minute continuous ejection, all nozzles

performed ejection

B: During 30-minute continuous ejection, all nozzles performed ejection, but satellites resulted

C: During 30-minute continuous ejection, some nozzles performed no ejection

[0125]

Layer Strength: The strength of the cured layer was evaluated employing a finger nail scratch test

A: The layer was not removed by scratching

B: The layer was removed somewhat by scratching

C: The layer was easily removed by scratching

[0126]

Contact Adhesion Property: The image printed surface, prepared as above, was subjected to cross-cutting of 11 longitudinal and lateral lines at an interval of 1 mm in accordance with JIS K 5400 to form 100 squares having a side length of 1 mm. Thereafter, Cellotape (registered trade mark) was adhered on the cross-cut surface. Subsequently, the Cellotape was rapidly pulled at an angle of 90 degrees and the remaining printed images, not peeled off, or the state of the cross-cut surface were evaluated based on the criteria below. The image printed surface which was not

subjected to the aforesaid cross-cut was also evaluated in the same manner.

[0127]

A: Employing the cross-cut test method, no printed images were peeled off

B: In the cross-cut test, printed images were slightly peeled off, while when the image surface was not cut, almost no peeling was noticed

C: Under both conditions, the image surface was easily peeled employing Cellotape (registered trade mark).

[0128]

Solvent Resistance and Water Resistance: A sample prepared by printing images onto a film was immersed in alcohol at 50 °C and warm water for 10 seconds, and image damage and the degree of contraction were visually evaluated based on the criteria below.

[0129]

A: No changes were noticed

B: Slight damage and contraction were noticed

C: Marked damage and contraction were noticed

Table 3

Ink Printer Matter	Cura- bility	Stability			Layer Strength	Close Contact Property	Solvent Resis- tance	Water Resis- tance
		Oxetane Ring Containing Compound	Ink	Ejec- tion				
Present Invention 1	1	A	A	A	A	A	A	A
Present Invention 2	1	A	A	A	A	A	A	A
Present Invention 3	1	A	A	A	A	A	A	A
Present Invention 4	1	A	A	A	A	A	A	A
Present Invention 5	1	A	A	A	A	A	A	A
Present Invention 6	1	A	A	A	A	A	A	A
Present Invention 7	1	A	A	A	A	A	A	A
Present Invention 8	1	A	A	A	A	A	A	A
Comparative Example 1	6	A	A	B	C	C	C	C
Comparative Example 2	6	A	A	B	C	C	C	C
Comparative Example 3	4	A	A	C	B	B	B	B
Comparative Example 4	6	A	A	B	C	C	C	C
Comparative Example 5	6	A	A	B	C	C	C	C
Comparative Example 6	6	A	A	B	C	C	C	C
Comparative Example 7	6	A	A	B	C	C	C	C
Comparative Example 8	4	A	A	C	B	B	B	B

[0131]

As can clearly seen from Table 3, curability, ejection stability of nozzles, layer strength, contact adhesion property of printed images, and solvent resistance as well as water resistance of printed images were superior to the comparative samples.

[0132]

[EFFECTS OF THE INVENTION]

According to the present invention, it is possible to prepare an actinic radiation curable ink which results in sufficient strength of the cured layer, excellent curability, stability of oxetane containing compounds as well as stability of the ink, and further excellent ejection stability of nozzles. Further, printed matter recorded by employing the ink-jet ink of the present invention exhibits excellent close adhesion property of printed images and excellent solvent resistance as well as excellent water resistance.

[NAME OF DOCUMENT] Abstract

[SUMMARY]

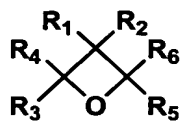
[PROBLEMS TO BE SOLVED]

An objective of the present invention is to provide an actinic radiation curable ink-jet ink which results in excellent photopolymerization, exhibits excellent curability as well as excellent stability of a compound having an oxetane ring and ink itself, results in sufficient strength of the cured layer, and exhibits ejection stability at the nozzles, excellent close adhesion property to the substrate, and excellent solvent resistance as well as water resistance, and printed matter using the same.

[MEANS TO SOLVE THE PROBLEMS]

An actinic radiation curable ink-jet ink comprising an oxirane group containing compound in an amount of 10 - 50 percent by weight, an oxetane ring containing compound in an amount of 50 - 90 percent by weight, and a vinyl ether compound in an amount of 0 - 40 percent by weight, an actinic radiation curable ink-jet ink wherein said oxetane ring containing compound is represented by General Formula (1) described below:

General Formula (1)



[SELECTED DRAWINGS] None